

WEATHERHEAD

Analysis of Asphalts

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ANALYSIS OF ASPHALTS

BY

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

DRURY LEE WEATHERHEAD

ENTITLED ANALYSIS of ASPHALTS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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Analysis of Asphalts.

Introduction.

Natural bitumens occur quite widely distributed in nature in various forms. They are not chemical entities but mixtures of hydrocarbons chiefly, with very small amounts, at times, of sulphur, nitrogen and oxygen derivatives. As these bitumens are of considerable importance commercially, a study of their nature and of methods of testing them is of value to the industries in which these bitumens find use.

There are several kinds of bitumens but only those known by the general name of asphalts enter into this discussion. These asphaltic materials are divided into classes according to their use, nature and origin.

Natural asphalts are the really true asphalts and are found in large deposits in nature, notably in Venezuela, the island of Trinidad, Persia and various other places. In these deposits the asphalt is associated with foreign matter, coarse stones, water and fine mineral matter, and it is necessary to introduce a refining process which removes these foreign substances and makes the material suitable for use commercially.

Other sources of bitumenous material are the residuums from the distillation of some varieties of petroleum oil. In the manufacture of artificial asphalt a hard solid bitumen such as gilsonite is tempered with a lighter liquid bitumen such as the petroleum residues mentioned above ^{the} or more liquid natural asphalts. As the petroleum residues are of three general classes, those with paraffine base, those with asphaltic base and those with a base

composed of a mixture of paraffine and asphaltic substances, artificial asphalts derived from their use are of very different composition.

Other commercial products of these bitumens are the asphaltic paints, roofing papers and preparations to fill in between bricks or wooden blocks in pavement.

As these natural bitumens find such important uses in the commercial world and as they are not definite in composition but quite variable as to constituent substances and relative proportions of the same it is highly desirable to have some way to examine these materials that will satisfactorily throw light on their proportional composition.

This field has been quite extensively investigated but there is still opportunity to throw more light upon the character of the asphalts and to devise better methods for testing them. It is definitely known that asphaltic substances are made up chiefly of hydrocarbons, at times associated with small amounts of their derivatives. Turning to organic chemistry we see that there is a large number of different kinds of hydrocarbons; as saturated and unsaturated; paraffine, polymethylene etc., and that mixtures of these might vary widely in physical and chemical properties. Investigation has shown that the hydrocarbons in asphalt vary considerably and that the nature of the asphalt as well as its resistance to wear and corrosion when used in pavements varies somewhat with the character and relative amounts of the hydrocarbons present.

Several different ways of approaching the testing of such substances naturally suggest themselves. The ultimate analysis of the material might at first be considered of prime importance. Many investigators worked in this direction but it is found that such

analysis does not throw much light on the real nature of the substance in question and is of value only in connection with other tests. Again, the fractions which might be obtained on distillation as well as the residue left after high temperature treatment might show to some extent the nature of the substance. The difficulty in this method of procedure is that when heat is applied the nature of the substances present may be greatly altered, especially by what is known as " cracking " of the heavier hydrocarbons. This method has been worked on to a large extent but is not relied on at present, as experience has shown that it sheds little real light on the character of the substance under investigation. This method is applied now only to the extent of finding the fixed carbon and the loss at certain temperatures. Another method of approaching this problem is a quantitative study of the physical properties; the specific gravity, softening point, melting point, penetrability, color, streak, odor, flowing test etc. These all tend to show the consistancy of the substance and may indicate its probable wearing qualities but do not show the chemical nature. The method, which perhaps, more than any other tends to show the chemical nature of the bitumen is that of determining the solubility of its constituents in various solvents. This method would naturally be expected to show better than any other at least the relative amounts of various classes of substances present.

The fact of the matter is that none of the above methods, alone, is considered entirely trustworthy and a combination of one or all of the above is usually employed to acquire a knowledge of the character of the substance.

Another point that the foregoing tests throw little light on is as follows. In artificial asphalts, asphaltic paints, papers,

fillers etc the substances used to temper the hard bitumens are of various kinds. The petroleum residues are composed of hydrocarbons of the paraffine series, of the polymethylenes and of mixtures of these two different hydrocarbon series: saturated and unsaturated members of both being present. Also coal tar residues, alone or mixed with petroleum residues, may be used to temper the hard bitumens. The character of the final product varies with the nature and amounts of tempering substances used. It is very desirable then to be able to tell, if possible, whether petroleum residues or coal tar residues were used as tempering substances and what quantities were used in either case. For this purpose use is made of the action of sulphuric acid on paraffines. Also tests for substances characteristic of coal tar are used, as for anthracene, phenols, cresols etc.

These tests, to a large extent, are not absolute and do not give very good quantitative results. The testing based on relative solubility in various solvents varies considerably and, as at present carried out, is open to improvement. It consists in extracting the substance for a comparatively long time with various portions of a solvent until all matter soluble therein is removed. This amount is determined by loss in weight. In this work we sought to improve the above method by the general principle of first dissolving the substance as completely as possible and then precipitating out the portions insoluble in different media.

Before going into a description of this method it might be well to review briefly the history of the subject so that a comparison may be drawn between these older methods and the new one to be proposed.

Historical.

This subject first attracted scientific investigation in

1837, when J. B. Boussingault⁽¹⁾ published a memoir on the nature of bitumens. He studied the action of a few solvents and of heat on some of them. At a temperature of about 230°C he found that an appreciable quantity of the substance distilled over. He designated this as "petrolene." The residue he called "asphaltene." He also tried the solvent action of alcohol and ether on the bitumens and found that part dissolved, leaving a residue almost entirely soluble in turpentine. He applied the term "petrolene" also to the portions soluble ⁱⁿ alcohol and ether and "asphaltene" to the residue. Le Bel and Muntz went over practically the same ground, but making more use of solvents; and in 1883 Le Bel⁽²⁾ added a few more facts in this direction.

At first petrolene and asphaltene were considered simple substances but it did not take long for organic chemistry to show that they were mixtures of paraffines, iso-paraffines, olefines, benzenes and additive benzenes and many other abundant and less known substances. Boussingault, from ultimate analysis, gave "petrolene" the formula $C_{80}H_{64}$ (C = 6) and pointed out that it was isomeric with the turpenes. He gave asphaltene the formula $C_{80}H_{64}O_6$ (C = 6) (O = 8).

Many other investigators have taken up the study of asphalt among them Clifford Richardson⁽³⁾, Laura A. Linton⁽⁴⁾, Dr. Henry Siffmann, Dr. Samuel P. Sadtler⁽⁶⁾, Dr. De Smedt, Peckman and others. The work of all of these will not be taken up here but just enough to show the general principles involved and the extent to which this problem has been worked out.

The solvents ordinarily used for petrolene are petroleum spirit, ethyl ether, alcohol, acetone and coal-tar benzenes. Those used most for asphaltene are carbon disulphide, chloroform, boiling oil of turpentine and benzol.

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Laura A. Linton⁽⁴⁾ worked to determine whether petroleum ether, California naphtha and ethyl ether are interchangeable solvents for petrolene; and turpentine, carbon disulphide and chloroform interchangeable solvents for asphaltene. This was done in the hope of leading to a method of analysis applicable to all asphalts and also to reveal something of the real nature of petrolene and asphaltene. She found that these solvents could not be used interchangeably. She found chloroform the most complete solvent while carbon disulphide and hot turpentine were almost equal in solvent power but not up to that of chloroform. Cold turpentine was not found to be as good a solvent as hot turpentine. She decided that the petrolenes and asphaltenes from different asphalts by the same solvents were dissimilar in nature and those from the same asphalt with different solvents were also different. The method of separating the petrolene and asphaltene was somewhat as follows. A sample of about five grams of the asphalt was put in an Erlenmeyer flask of appropriate size, fifty cubic centimeters of petroleum ether added and the mixture allowed to stand over night. It was then filtered on a balanced filter, retaining as much of the bitumen as possible in the flask. Twenty-five cubic centimeters of the solvent was poured into the flask and allowed to stand for about three hours with frequent agitation if possible. This was decanted on the same filter, another portion of the solvent added and so on until the solvent added to the residue ceased to be colored, which often necessitated a half dozen extractions. All the residue was then transferred to the filter, washed well, dried and weighed and then replaced in the funnel. The funnel used was provided with a stopcock which was closed and hot turpentine added to cover all the residue. After about three hours of digestion the stopcock was opened and the filter drained, the stopcock again closed,

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a second portion of hot turpentine added. This was repeated until the turpentine came through clear. The residue was dried and weighed again. It was then extracted in the funnel with chloroform as with turpentine, the residue being dried and weighed.

The portion extracted by the petroleum spirit was called petrolene, that by the other solvents asphaltene. Thus a fractionation of the asphaltene was acquired which she considered of value. The residue from extraction was composed of non-bitumenous organic matter and mineral matter. This was ignited and the loss ascribed to the organic matter. If calcium carbonate was present it was found necessary to recarbonate the ash with ammonium carbonate.

Other methods of extraction have been used. Very often the asphalt was treated in an open beaker at room temperature or on a water bath with successive quantities of solvent until all soluble material was removed.

Reflux condensers and the Soxhlet apparatus have been used and are considered by some to be very satisfactory while others say that in case naphthas and petroleum spirits are used some of the more volatile portions are always lost; also too high heat may alter the character of the hydrocarbons originally present. Furthermore a slight amount of very fine mineral matter in suspension may go through with the solvent. With a Soxhlet extractor the sample is usually weighed into a tared Gooch crucible with an asbestos felt in the bottom and sometimes mixed with sand. The apparatus is then arranged so that the solvent percolates through the sample. This is continued until upon three hours extraction the sample does not loose over two milligrams in weight.

Sadtler⁽⁶⁾⁽⁹⁾ dissolved the petrolene with acetone, the asphaltene with chloroform, using a reflux condenser arrangement. He extracted

for twelve hours with acetone and for eight hours with chloroform.

Endemann⁽⁷⁾ extracted with chloroform in a flask, filtered, evaporated off the chloroform and distilled the residue getting the amount of petrolene and asphaltene in that way.

Some have analysed asphalt as coal is often analysed; for volatile matter, ash, fixed carbon and sulphur. But this is not considered of much value. The amount of sulphur^{varies} quite a bit in all asphalts. As it has an influence on the character of the asphalt, if present in large quantities, it is of importance. It is determined by the usual methods.

The moisture in natural bitumens is largely in a hygroscopic condition. It is most often determined, if determined at all, by heating a sample to 100°C for some time. Laura A. Linton says that a considerable loss is sometimes brought about in this way and that heating at 50°C is more desirable as all water may be driven off without losing the more volatile parts of the bitumen. Most investigators are satisfied with the heating at 100°C as the loss of volatile constituents is negligible in most instances at least. Some dry in vacuo over sulphuric acid while others deem this unnecessary.

Clifford Richardson⁽³⁾ has done a great deal of work with asphalts. He has taken up the physical properties as well as the chemical properties and the ultimate analysis and has made quite a study of the nature of the constituents, for, quoting the above author, " the relative proportion of the various series which are present in any petroleum or solid bitumen has a strong influence on its characteristics and more especially the relation of the saturated to the unsaturated hydrocarbons and of the paraffines to the polymethylenes, these considerations being quite apart from the relative amounts of liquid and solid substances, malthenes and asphaltenes,

upon which the consistancy of the bitumen, but not its chemical characteristics, are based."

He has decided that the characterization of these bitumens is ascertained by determining the relative portions of malthenes and asphaltenes, the proportions of saturated to unsaturated hydrocarbons in the maltlenes and the characteristics of these malthenes. He has practically substituted the term maltlene for petrolene. From his study of the nature of bitumens he concludes that natural bitumens are such complicated mixtures of various hydrocarbons and their derivatives that it is impossible to separate them completely into their individual constituents and to thus differentiate them and characterize them. Their physical properties must then be considered and attempts made to separate the proximate constituents into various classes according to their solubility and their behavior toward reagents, which, with determinations of the amount of fixed carbon they yield on ignition and their ultimate composition should throw light on the nature of the bitumens. He determines the fixed carbon as it is usually done in coal analysis, sulphur by any common method and the ultimate composition in the usual way. The physical tests cover a wide range and are as follows. The specific gravity of the original substance and pure bitumen at $78^{\circ}/78^{\circ}$ F., color of streak and powder, luster, structure, fracture, hardness, odor, softening point and flowing point. A penetration test is also carried out which depends on the depth to which a standard needle will sink in the substance at a certain temperature. For fluxes he also determines flash point and viscosity. He makes many tests of a chemical nature to show the character of the constituent substances. He determines the loss ~~of the~~ of the original substance at 212°F for one hour, the loss of the dry substance at 325°F for seven hours and the penetra-

bility of its residue; the loss of the dry substance at 400°F for seven hours and the penetrability of its residue. The solubility in carbon disulphide, the non-bitumenous organic matter and inorganic mineral matter is obtained. The solubility of the bitumen in 88° naphtha giving the so-called " Malthene ", the amount of this malthene removed by sulphuric acid, and the amount soluble in 62° naphtha are the tests made on malthenes. He calls the substance soluble in carbon tetrachloride asphaltene and that not soluble in cold carbon tetrachloride but soluble in carbon disulphide, carbenes. He found that the amount of bitumen soluble in naphtha depends to a large extent on the density of the naphtha employed. He extracted the bitumens in the cold, in Erlemmeyer flasks by a method simialr to that one used by Laura A. Linton described before. He found it better to extract at room temperature as the use of heat in extraction caused variations in the results. His extractions were all by this general method.

In October 1908 J. Marcusson and R. Eichmann⁵ submitted an article covering investigations to determine whether or not a bitumen is a natural asphalt or an artificial one in the preparation of which petroleum residues or coal-tar may have been used. They point out that use has been made of the fact that natural asphalts contain a much higher percentage of sulphur than petroleum residues. This has been made use of in determining whether a product was a natural or an artificial substance. These authors point out that this does not give a very satisfactory distinction as mixtures of natural asphalt and petroleum residues up to large percentages of either constituent could not be distinguished from either of the pure substances. They proposed a distinction by the determination of the paraffine in the two substances. The basis of this is that, accord-

ing to them, natural asphalts contain very little or no paraffine while petroleum residues contain a relatively large amount. To make this determination they extract ten grams of the material with benzol and when solution is as complete as possible the solution is poured into two hundred cubic centimeters of petroleum ether, shaken and filtered. The filtrate is treated three times with fifteen cubic centimeters of sulphuric acid in a separatory funnel, shaken with alcoholic potash and then with water. The solvent is then evaporated and the residue dried at 105°C and weighed. This product shows notable differences according to the nature of the original material. The authors give the properties of this residue as obtained from different substances. The percentage yield also varies with the starting substance. If much paraffine is present vaseline-like particles appear distributed throughout the residue. To determine the amount of paraffine the residue is treated with alcohol-ether mixture (1=1) and after solution is complete as possible it is separated from any oily residue and then cooled to -20°C ; in other words the Engler-Holde method for paraffines is applied. Petroleum residues show 3.3 - 16.6 per cent paraffines while natural asphalts give very little, 2.2 - 6.3 per cent of a resinous substance containing some paraffines. To get a better distinction these investigators distill the residue from the solution in petroleum ether and treat the distillate for paraffines. This shows a wider distinction between natural and artificial asphalts. They also state that the sulphur in natural asphalts raises by this treatment to 3.5 - 35.0 per cent. Steam led through this distillate from petroleum residues gives hydrogen sulphide while steam sent through this distillate from natural asphalt gives no trace of hydrogen sulphide.

To detect coal-tar adulteration these investigators made

use of tests for characteristic substances constantly present. The odor, high content of free carbon (21 % or over), anthraquinone test and behavior of distillate towards sulphuric acid are taken into account. Grafe's diazobenzol chloride test is also considered of use.

Fatty pitches are detected by the Acreolin test, saponification number and acid number. These investigators take it for granted that all petroleums are of paraffine base. It is probable then that their method might not be very satisfactory in a region where petroleums have asphaltic base.

In 1907 Mr. W. H. Leverette, under the direction of Prof. S. W. Parr started a new method for the analysis of asphalt. The problem of determining the nature of the constituent parts of the bitumen was approached by a different method than used by any of the preceding investigators. The idea in this method was to dissolve the bitumen as completely as possible and then to precipitate out portions by partial solvents.

To this end a study was made of the relative solvent powers of several organic liquids. Gilsonite was used for the bitumen and the most complete solvents were found to be chloroform, carbon disulphide, carbon tetrachloride, hot turpentine, benzol and toluol. Carbon disulphide was selected as solvent for the bitumen as it completely dissolved the sample used. The solution was mixed with one hundred cubic centimeters of ligroin and shaken. The precipitate was filtered on a Gooch crucible with an asbestos felt, dried in an atmosphere of carbon dioxide and weighed. The filtrate was concentrated to a suitable volume and then thirty cubic centimeters of a mixture of two parts methyl alcohol and one part acetone was added and well shaken. The precipitate thus formed was filtered off

as before, dried and weighed. An excess of water was added to the filtrate in a large separatory funnel and allowed to stand until the emulsion formed at first had cleared up. A separation of the water and the layer of oil was then made and the oil collected, dried and weighed.

It would seem, therefore, from this resumé of investigation on asphalts that while there is a general agreement as to the complex nature of the substance, there is also an agreement to the effect that the constituents divide themselves into two or three groups of substances which are quite distinct in their physical properties at least. There is a general recognition, moreover, of the fact that upon the relative quantity of these group constituents which have been variously designated as asphaltenes, petrolenes, malthenes etc depends the ultimate character of the material. The investigations as above outlined then have been mainly concerned in the quantitative estimation of the amount and character of these substances.

Experimental.

The experimental work to be described is a continuation of Leverette's investigation and is an attempt to more sharply define these components and devise a method which would result in the ability to determine the percentage values within a much narrower range of variation than has been possible heretofore.

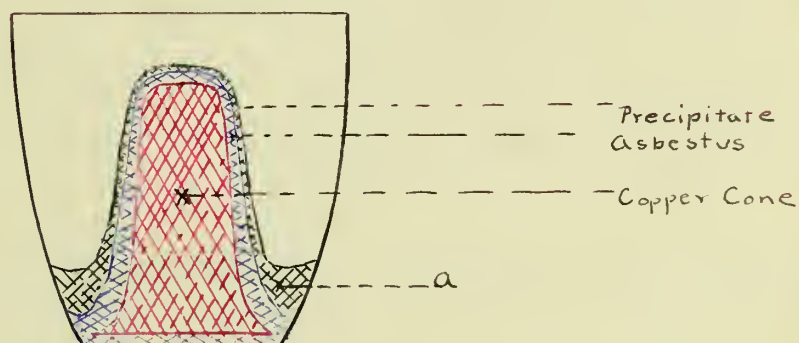
A sample of pure gilsonite was worked on until the method of operation was established, a large amount of work being done in the way of trials for various solvents and with different kinds of apparatus and methods of procedure. After some experiments with solvents, chloroform and carbon disulphide were selected as the most complete solvents, it being found that they dissolved practically all of the sample in use. Half gram samples of the powdered gilsonite

were weighed into a scoop of polished aluminum and transferred to short stemmed separatory funnels of about two hundred and twenty-five cubic centimeters capacity. Various trials showed that five cubic centimeters of solvent was most convenient to use. This was added and when complete solution had taken place one hundred cubic centimeters of Kahlbaum's ligroin, specific gravity 0.7162 (24.5 C/24.5) was added and the mixture shaken. After standing for two hours the mixture was filtered through a Gooch crucible with an asbestos felt prepared in the usual way. When filtration was complete the precipitate was washed with ligroin, dried in an atmosphere of carbon dioxide at 105°C and weighed. When constant weight was obtained on several samples they were heated at about 105°C in the air to see if any oxidation took place. None could be detected by change in weight so thenceforth the precipitates from this step were dried in an ordinary oven at about 105°C. It was found that Gooch crucibles prepared in the ordinary way were unsatisfactory for this purpose as, if the asbestos felt were too thin some of the precipitate would go through and if too thick great difficulty was experienced in filtration and very often with a medium sized filter the precipitate would so clog it that filtration would be very tedious or impossible. It was then decided to filter on a small Büchner funnel with an asbestos bottom. The filtration was comparatively easy by this process. The precipitate in the funnel was well washed and then dissolved in boiling benzol. The benzol solution was then transferred to a weighed dish, the benzol evaporated off and the residue weighed and called Precipitate 1.

This process was considered unsatisfactory as it involved a good bit of manipulation and afforded much opportunity for loss. It was also difficult to dissolve all of the precipitate out of the

Figure I

Gooch Crucible for Asphalt Filtrations



asbestos.

A new method of preparing a Gooch crucible for such filtrations ^{at the suggestion of Dr. Mears} was then hit upon. The Gooch was prepared as follows. A thin layer of asbestos was put in the bottom of the crucible in the usual way. A cone of porcelain or platinum or other metal gauze was then set securely on this and covered with the prepared asbestos so that a mound reaching almost to the top of the crucible was formed. The surface of this cone and bottom of the crucible thus offered a much larger surface for filtration. A Gooch prepared in this way is illustrated in Figure 1.

In filtering it was found best to introduce the liquid near the side so the precipitate would collect in the groove thus leaving a free surface for the remaining portions to go through. Using a Gooch prepared in this manner it was found easy to filter off the precipitates obtained. Cones of copper gauze were used in these experiments.

It was thought that perhaps the temperature would affect the precipitation. The dropping funnels were then set in a freezing mixture for three hours just after adding the ligroin. This procedure was found to be unsatisfactory as precipitation seemed very incomplete and variable under these conditions.

The freshly precipitated solutions were then boiled one hour over a water bath, using a reflux condenser. It was found in this case that the results were more concordant but about ten per cent lower than those obtained at room temperature which gave a precipitate of about twenty-five per cent of the gilsonite.

This suggested that the ligroin changed specific gravity by loss during boiling and that its solvent power changed with the specific gravity. This was found to be the case. It became evident

then that a liquid of more constant composition than ligroin would give more concordant results.

Next the effect of shaking was tried. The freshly precipitated samples were put in a shaker and shaken for from three quarters to one hour. This seemed to have no effect, either on the character, or quantity of the precipitate.

A commercial product known as Hexane was selected as a more suitable precipitating liquid. This is ^a product from petroleum distillation furnished by the Standard Oil Co. It is composed of various hydrocarbons of about the same specific gravity and boiling points as shown in the table below, obtained by the following procedure. Two hundred and fifty cubic centimeters of hexane was measured out and its specific gravity taken by a Westphallbalance. Air was then blown on the liquid until there was about two hundred cubic centimeters left. The specific gravity of this was then taken in the same way and so on until sixty cubic centimeters was left. The specific gravity did not change very much as is shown by the table.

cc Hexane.	C. Temperature.	Specific Gravity
250	23	0.6516
196	20	0.6569
150	20	0.6622
100	18	0.6698
60	23	0.6740

This was found to give a much higher but more constant precipitate.

As carbon disulphide vapors are poisonous and somewhat disagreeable to work with, and also very explosive experiments were tried using chloroform as original solvent. This was found to work very well and the results though fairly concordant, to our surprise were

about seven per cent lower than those with carbon disulphide. We then continued the use of carbon disulphide as solvent.

Shaking was also tried as with the samples in which ligroin was used but seemed to have no effect.

The filtrate from the first precipitation was then evaporated to about twenty-five or thirty cubic centimeters and then put in a five hundred cubic centimeter separatory funnel of the same type as those used in the first step. Three hundred cubic centimeters of a mixture of two parts methyl alcohol and one part acetone by volume was added and the mixture shaken thoroughly. The mixture was then filtered on one of the specially prepared Gooch crucibles. It was found that the precipitate adhered to the walls of the funnel and could not be washed out by the precipitating liquid. This had to be dissolved in hexane, precipitated and filtered. It was found necessary to repeat this several times in order to get all the precipitate out as it was rather sticky. The precipitate was then dried in an atmosphere of carbon dioxide at 105°C and weighed. When several of these precipitates had been thus obtained they were heated for long periods in air at 105°C . No oxidation could be detected and so afterwards all these precipitates were dried in the ordinary drying oven.

The above method of precipitation was not considered satisfactory for several reasons. First it seemed better to have a definite volume of liquid containing the bitumen each time. Then the many re-solutions and reprecipitations took too much time. The following method was then adopted.

The filtrate from the first precipitate was evaporated as nearly as possible to dryness on a water bath recovering the hexane by a condenser. After cooling, ten cubic centimeters of hexane were

added and allowed to stand until solution took place. Some bitumen usually remained which the hexane would not redissolve. In the beginning it was thought that the gilsonite was dissolved in so small an amount of carbon disulphide that when one hundred cubic centimeters of hexane were added all the material insoluble in hexane would be precipitated. The difference in the amounts of precipitates given by chloroform and carbon disulphide however suggested that perhaps an application of the Phase Rule entered in here and that we were really dealing with a ternary mixture and did not have a case of simple solution. This residue obtained then seemed to confirm this view so the following procedure was added. After the filtrate from the first precipitation had been evaporated to dryness it was taken up with fifteen cubic centimeters of hexane and allowed to stand a while. It was then filtered through the same filter used at first and washed well. This filtrate was then evaporated to dryness and taken up with ten cubic centimeters of hexane and used for the second precipitation.

The method of making the second precipitation was as follows. Three hundred cubic centimeters of the precipitating mixture was put in an ordinary seven hundred and fifty cubic centimeter beaker and stirred well with a rod. The hexane solution was then allowed to drop in slowly, the stirring being continued all the time. As soon as all the filtrate from Precipitate 1 had been washed in, the mixture was filtered on a Gooch prepared as described before. Some precipitate adhered to the beaker and the rod. This was dissolved in a little hexane as possible, five to ten cubic centimeters, and reprecipitated by about one hundred and fifty cubic centimeters of the mixture, shaking all the time. This was filtered on the same filter. Any precipitate still remaining was dissolved in hexane or tol-

uene and transferred to a small weighed glass dish, dried and weighed. The gain in weight of the crucible and dish together represented the second precipitate.

It was thought desirable to change this second precipitant liquid for one of constant composition. This was done as good acetone is quite expensive and it was thought that any other liquid which dissolved a portion of the bitumen large enough to give a good separation would be as suitable. Methyl alcohol(sp. gr. 0.794 at 16°C) was selected for this purpose and found satisfactory. The method of precipitation was carried out as before.

The filtrate from the second precipitation was then treated with a large quantity, one to two liters, of water and allowed to stand until the emulsion first formed cleared up. A separation of the liquids was then made and the asphaltic oil washed into a weighed glass dish with hexane, the hexane evaporated and the residue heated to constant weight in an atmosphere of carbon dioxide at 105°C. These precipitates were also heated in the air to see if oxidation took place. None was detected so therefore these precipitates also were dried in the oven at 105°C.

It was discovered that sometimes it took a comparatively long while for the emulsion to clear up and the procedure was more or less troublesome. As the entire bitumen was obtained in these three precipitates it was decided to simply evaporate off the methyl alcohol in the filtrate from the second precipitation and weigh the residue. This was found a satisfactory procedure as the methyl alcohol could thus be recovered by use of a condenser, distilling from the dropping funnels directly, using a steam bath to heat the solution. This procedure, of course, is open to the objection that any foreign matter collecting in the filtrate or dissolved in the alcohol would thus be

included in the precipitate. This did not prove to be a very serious objection, however.

In all cases where it was necessary to wash a precipitate into a dish with a solvent and then evaporate off the solvent it was found that the precipitates parted with the last trace of the solvent with difficulty. The first heating of the precipitates, after evaporating off the hexane, was carried on for from four to six hours. Each successive heating was continued for three or four hours. When the precipitate did not loose over a milligram after such heatings it was considered to be of constant weight. In case of the second precipitates it seldom took over seven or eight hours of drying while in case of the third precipitates about ten or twelve were necessary.

Work was carried on to determine the effect of standing on the first precipitates. By various trials it was found best not to filter sooner than two hours after precipitation. At the end of this time filtration could be effected without much difficulty. It, however, it was convenient to allow the precipitate to stand longer, up to forty-eight or seventy-two hours, it filtered very much more easily. The particles of precipitate seemed to grow much larger on standing and filtration was very much ^{more} easy to accomplish. This standing was not necessary, however, as results showed complete precipitation within two hours; but the precipitate was handled so much more easily that when ever convenient it was preferred to let the precipitates stand over night at least. In the case of precipitate two it was always filtered immediately ^{before settling out, being gummy in character,} so that as much of the precipitate as possible could be transferred to the crucible.

All filtrations were carried out using suction in the usual way with Gooch crucibles. Ordinary filtering flasks were used and the filtrates rinsed back into the dropping funnels. Another procedure

was adopted for a while. A second funnel, clamped to an iron stand, was used to receive the filtrate; having a two-holed stopper in its mouth bearing the Gooch funnel and ^a tube leading to the pump. This procedure was not continued, however, as the first was considered satisfactory.

At first tall beakers were used for the first precipitation with the idea that the filtrate would be transferred to the Gooch crucible before the precipitate, and the precipitate would also be washed by decantation. This was unsatisfactory, however, as much evaporation took place. A large weighing bottle with a cap fitted over the outside was then employed. This, too, was unsatisfactory. In the case of separatory funnels the precipitate naturally reaches the filter first, which in a way is an objection. However, in cases, especially where ^{the} precipitate had stood over night, it was found that if the mixture was handled gently just before filtration that the filtrate would run through the precipitate, most of which remained in the funnel. Then after the filtrate had gone through the precipitate would be washed into the crucible. This procedure was very satisfactory.

The method then resolved itself into the following three stages. The one gram sample was dissolved in five cubic centimeters of carbon disulphide, one hundred cubic centimeters of hexane added, shaken well and allowed to stand at least two hours. It was then filtered on a Gooch and the filtrate evaporated to dryness and taken up with fifteen cubic centimeters of hexane, cooled, allowed to stand fifteen minutes or more and refiltered on the same Gooch.

The filtrate was evaporated to dryness and after cooling ten cubic centimeters of hexane added. This solution was allowed to drop slowly into two hundred cubic centimeters of methyl alcohol which was being stirred well all the time, filtered, transferring

as much precipitate to the crucible as possible. The residue on the rod and in the beaker was redissolved in five to ten cubic centimeters of hexane and reprecipitated with one hundred and fifty cubic centimeters of methyl alcohol, the liquid in the beaker being continually rotated. This was filtered as before and the residue in the beaker transferred to a weighed glass dish by use of hexane.

The filtrate from the above process was evaporated until only a heavy dark oil was left. This was washed into a weighed dish by hexane or toluene, dried and weighed.

The above procedure was followed in the cases where practically all the substance was soluble in carbon disulphide. Where this was not true, another precipitate was obtained by filtering off the portion insoluble in carbon disulphide. This gave the amount of non-bitumenous organic matter and mineral matter. An ash determination gave the amount of mineral matter and by difference the non-bitumenous organic matter was obtained.

Data and Results.

The material used to work out the method was No. 1 " Sarco Gilsonite " furnished by the Standard Asphalt and Rubber Co., shipped directly from Independence, Kansas. This material was a solid bitumen, black and shiny in mass but giving a light brown streak and powder. This was pulverized and put through a sixty mesh sieve. As preliminary tests its ash was determined and found to be practically nothing. Its solubility in chloroform and carbon disulphide was determined with the following results.

Wt. Sample.	Solvent.	% insol. Material.
7.5	CHCl_3	0.068
7.5	CS_2	0.080

The samples were weighed out on watch glasses and transferred to separatory funnels and forty cubic centimeters of solvent added and allowed to stand for twenty-four hours. Gooch crucibles were prepared with a felt of asbestos about one half inch thick. The solutions were filtered and washed with the solvents. This amount of insoluble material was neglected in further determinations as it was small and would necessarily come out with the first precipitate. After experimenting with various quantities of the Gilsonite one gram samples were found most satisfactory. Results are given in Table 1.

A petroleum residue called " Sarce Petrolene ", also furnished by the Standard Asphalt and Rubber Co., and used to temper the gilsonite in making asphalt cements and fillers, was next analysed in the same way. This was a shiny black, viscous liquid with a so-called earthy or asphalt odor. Samples of about one gram were weighed out by difference. It was found very desirable in the case of this sample to allow Precipitate¹ to settle at least twenty-four hours. Results are given in Table 2.

A mixture was then prepared from these substances by mixing equal weights in a casserole. This mixture was allowed to stand in a warm place over night and then heated on a sand bath until the mass became a homogeneous liquid. It was stirred well, small bubbles of gas being given off which looked blue in air and had a characteristic asphalt odor. When solution and mixture seemed complete the mass was allowed to cool. The mixture was a black, shiny, firm mass, somewhat rubbery in thin strips. It was designated Mixture 1. For analysis pieces were cut from the mass and one gram samples weighed out on a polished aluminum scoop and transferred to the separatory funnels. Results are given in Table 3.

Mixture 2 was prepared in the same way as Mixture 1, using

three parts " Sarco Petrolene " and one of Gilsonite by weight. In this case solution was more easy and gas given off more readily so that heating was continued only about five minutes after the gas began to appear, this being long enough to give a homogeneous mass. This mixture was also a shiny black mass, quite soft and rubbery. To weigh out samples for analysis balls of this substance were made and put on a watch glass. These were weighed and removed, getting the weight by difference. Results are given in Table 4.

In the same way Mixture 3 was prepared by using two parts " Sarco Petrolene " by weight and one of Gilsonite. This mixture was rubbery but much more firm than Mixture 2. Samples for analysis were weighed out in the same ^{way} as in case of Mixture 2. Results are given in Table 5.

A light coal-tar pitch was next analysed. It had the characteristic tarry odor and was a black, shiny, viscous liquid. It was of the lighter and more fluid coal tars. It was weighed out by difference from a covered weighing bottle. Results of its analysis are given in Table 6.

Mixture 4 was prepared by weighing equal amounts of this coal tar, " Sarco Petrolene " and Gilsonite into a casserole and mixing them well. The mixture was treated as the others. On cooling it became a black mass, rubbery in consistency, much like Mixture 3, but easily distinguished from it by its tarry odor. All the other mixtures had the characteristic asphalt odor. Results of its analysis are given in Table 7.

Next a sample of Trinidad Lake asphalt cement, furnished by the Barber Asphalt Company was analysed by this method. A large portion of it was insoluble in carbon disulphide. After extracting over night with carbon disulphide the insoluble portion was filtered

onto a Gooch prepared as described before, and washed with carbon disulphide until the filtrate came through colorless. The filtrate was evaporated to five cubic centimeters and analysis of the soluble bitumen carried out as before. An ash determination was made in the usual way. After ignition at a red heat the weighed precipitates were treated with ammonium carbonate and found to gain no weight. Results are given in Tables 8, 9 and 10.

The material obtained as Precipitate 1 from each substance analysed was apparently the least volatile constituents. All these precipitates had about the same physical qualities. They were firm at 105°C and had no point where they became soft or viscous, black and could be powdered between the fingers when dry. There was not time to analyse these substances for ultimate composition, but from physical appearance and solubility they seemed to be closely related as to composition.

Not quite so close a relation seemed to exist between the substances obtained as Precipitate 2. In the case of Gilsonite this precipitate was sticky and fairly soft at 105°C but at room temperature would powder between the fingers. It did not have the jet black appearance of Precipitate 1 but had a brownish tinge. Precipitate 2 as derived from the other samples was sticky at ordinary temperatures and some samples flowed a little at 105°C when in glass dishes. This precipitate was doubtless the intermediate hydrocarbons.

Precipitate 3 probably contained the lighter and most volatile portions of the bitumen. At 105°C this was an oil with the appearance of dark machine oil but more viscous. It was solid but sticky at ordinary temperatures.

Some investigators have made use of the appearance of the petroleum spirit solution to determine the nature of the asphalt.

The appearance of the filtrate from Precipitate 1 is considered by us of importance. In the case of all the samples except the coal tar and the Trinidad Lake cement the filtrate had a sparkling, clear, wine colored appearance, while with the coal-tar and Trinidad Lake samples the solution seemed clouded and had a greenish fluorescence like native petroleum oil. This is doubtless of interest in a qualitative way. The fluorescence of the asphalt solution was much less than that of the coal-tar.

Table 1.
Gilsonite.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	48.17%	39.21*%	10.09%	97.47*%
2	47.64	42.62	9.14	99.40
3	45.64	43.67	11.30	100.61
4	47.18	42.92	9.88	99.99
Average	47.16	43.07	10.10	99.99 100.33

* Omitted from the average.

Table 2.
"Sarco Petrolene."

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	3.07*%	69.92%	27.94%	100.63
2	7.64	69.70	22.23	99.66
3	5.49	77.01	18.11	100.61
4	7.53	71.63	20.41	99.57
5	7.95	83.81	9.18*	100.44
6	4.90	75.44	19.04	99.38
7	7.50	82.32	9.65	99.47
8	6.93	72.15	20.51	99.59
Average	6.65	75.15	19.71	99.92 101.71

* Omitted from the average.

Table 3.
Mixture 1.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	27.48%	52.16%	20.48%	100.12
2	27.29	53.03	19.64	99.96
4	29.20	50.20*	16.42	95.82*
5	29.48	54.83	16.92	101.23
6	29.40	56.03	14.68	100.31
7	29.38	50.86	19.52	99.76
Average	28.71	53.38	17.97:	100.28 100.06

* Omitted from the average.

Table 4.
Mixture 2.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
2	17.83%	70.43%	12.29%	100.61
3	18.58	67.87	13.66	100.11
4	17.77	63.06	19.05	99.88
5	19.02*	59.37	22.15	100.54
6	18.71	65.59	16.86	100.16
7	18.52	66.39	14.36	99.27
8	18.28	56.92*	25.77*	100.97
Average	18.28	64.46	17.22	100.36 99.96

* Omitted from the average.

Table 5.

Mixture 3.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	20.03 %			
2	20.92 %	64.45 %	14.21 %	99.58 %
3	20.24	64.30	16.01	100.55
4	21.65*	63.59	14.73	100.17
Average	20.40	64.11	14.98	100.10 99.49

* Omitted from the average.

Table 6.

Coal Tar.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	18.63 %	39.54 %	17.17	75.34 %
2	18.78	40.38	26.72	85.88
3	19.06	40.69	22.69	82.44
Average	18.82	40.20	22.19	81.22 81.21

Table 7.

Mixture 4.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	26.29 %	45.08 %	24.60 %	95.97 %
2	27.74	51.45	16.39	95.58
3	26.38	48.10	22.15	96.63
4	24.13	50.43	22.04	96.60
Average.	26.13	48.76	21.30	96.19 96.19

Table 8.

Mineral Matter in Trinidad Lake Asphalt Cement.

Sample.	% Ash.
1	27.74
2	25.69
3	25.07
4	24.28
Average	25.69

Table 9.

Trinidad Lake Asphalt Cement.

Sample.	Insol. in CS ₂	Non-bit. org. matter. by Diff.	Ppt. No. 1.	Ppt. No. 2.	Ppt. No. 3.	Total.
1	29.89 %	4.20 %	16.96 %	39.44*%	13.94*%	100.23 %
2	28.82	3.13	18.99	33.19	18.67	99.67
3	23.94		18.81	36.82	20.56	100.13
4	27.21	1.52	16.04*	32.86	23.84	99.25
5	25.14		18.96	30.71	25.71	100.52
Average	27.00		18.43	33.39	22.20	100.10 101.02

* Omitted from the average.

Table 10.

Trinidad Lake Asphalt Cement Precipitates Calculated to Percentages of Material Soluble in Carbon Disulphide.

Sample.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
1	24.09 %	55.99*%	19.79*%	99.87 %
2	26.54	46.38	26.04	98.96
3	24.73	48.41	27.05	100.19
4	22.03	45.15	31.90	99.08
5	25.32	41.02*	34.34*	100.68
Average	24.54	46.64	28.33	99.75

99.51

In the case of Gilsonite we get the highest percentage of Precipitate No. 1 and the lowest percentage of Precipitate No. 3 obtained with any samples analysed; while with " Sarco Petrolene " we get the lowest percentage of Precipitate No. 1 and the highest of Precipitate No. 3. By taking the average of the percentages of the three precipitates obtained from Gilsonite and the tempering oil we get, theoretically, the percentage composition of Mixture No. 1. A comparison of the percentage by analysis and the theoretical percentages are given below.

Mixture No. 1.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
Theoretically	27.00%	59.11%	14.90%	101.01%
By Analysis	28.71	53.38	17.97	100.06

Though the actual analysis does not exactly agree with the theoretical, yet the same general division of the constituent hydrocarbons of the bitumen is seen.

For Mixture No. 2 a similar comparison is given below.

Mixture No. 2.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
Theoretically	16.93%	67.13%	17.31%	101.37%
By Analysis	18.28	64.46	17.22	99.96

Again a general likeness is seen although an exact agreement was not found.

A comparison in the case of Mixture No. 3 is more favorable.

Mixture No. 3.	Precipitate. No. 1	Precipitate. No. 2	Precipitate. No. 3	Total.
Theoretically	20.28%	64.46%	16.51%	101.25%
By Analysis	20.40	64.11	14.98	99.49



In this case a better agreement is obtained and shows that if the percentage composition, according to this method of analysis, of the hard bitumen and the tempering oil were known the proportions for tempering could be estimated with a fair degree of accuracy. It must be born in mind, though, that in making these mixtures a smoke was given off which may have contained some of the lighter constituents. Heating may also have caused " cracking " so that higher percentages of the less soluble portions may have been formed and also higher percentages of the most soluble constituents, thus lowering the percentage of the intermediate substances. In Mixture No. 3 the best agreement is shown and in the preparation of this mixture heat was employed less than in the case of the other mixtures and less gas was given off.

From the limited amount of data obtained on Trinidad Lake asphalt it seems that this method applies to this natural bitumen as well as to the artificial asphalts and coal tar. The percentages seem to show a different proportion than that shown with artificial mixtures, the first and third precipitates being more nearly equal than with the latter. It appears, then, that this method may give characteristic proportions for a natural asphalt. The main point to determine, however, is whether or not asphalts of different origin giving similar quantities of these precipitates are of like durability, stability etc. Investigation to show this is desirable.

Conclusions.

This method was derived to give a means of investigating the constituents of bitumen chemically. It was not intended that it should replace the physical tests or other examinations, but that it should be carried out with them, as it is believed that this meth-

od will indicate better than the others now in use, the chemical nature of the substance under examination. It appears from the analyses made that the amount of Precipitate No. 1 in an asphalt shows its degree of stability and hardness, while a high percentage of Precipitate No. 2 and especially of Precipitate No. 3 shows a soft asphalt. Engineering tests and experience, of course, are necessary to ascertain the value of this index, but, however, that may be, if these tests which give the relative amounts of the asphalt soluble in various solvents are of value, they can be best obtained by this method. The degree of tempering, if desired, may also be estimated after collecting a large amount of analytical data on solid bitumens like Gilsonite and on the various tempering oils.

By this method it seems that we will not only be able to determine the degree of tempering with asphaltic residuums but also the adulteration of asphalts with coal tar of varying consistancies. The above mixtures were prepared and analysed with this end in view. While this method seems a good ^{test} for coal tar adulteration, it is not intended to substitute it for the qualitative tests such as odor, color, anthraquinone etc, and specific gravity determinations which are of highest importance.

From a limited investigation it is shown that while coal tar may give a first precipitate approaching some of the mixtures of pure Gilsonite with tempering oils of an asphaltic base, in case Precipitate 2 there is a wide and easily detectable difference which seems to us of great value.

In applying this method to coal tar the results did not add up to one hundred per cent, probably due to the loss of water and most volatile constituents of this complicated mixture.

There, however, seems to be one factor which, at present,



we are unable to account for satisfactorily and have great difficulty in overcoming; namely, that while in case of Precipitate No. 1 results obtained the same day agreed closely among themselves, when these same results are compared with those obtained under similar circumstances at other times they fail to agree within, sometimes, an error of three per cent. This difference is usually less, however, and does not seem to be due to variation in temperature. This is shown especially in Table 3.

In all the other methods used to study the nature of the constituents of asphalt much time is lost in carrying out time-consuming extractions which are obviated by our method of attack. It also seems possible to obtain a better agreement of results with reasonable skill.

The apparatus used for this method is more simple and less expensive than that for Soxhlet extractions etc, which fact is another point in its favor. The set of insoluble portions which it gives we think of more engineering value than those obtained by extractions as usually carried out. The expense of reagents is not more than that in other cases, as the hexane and methyl alcohol are recovered and after purification may be used again. No high temperature is employed and therefore little or no chance is given for " cracking " in the original substance.

The method as it now stands, however, is in a more or less tentative state. As hexane is quite expensive and large amounts of it are used, some cheaper liquid might be found to replace it. Depending on the grade of accuracy desired in results, cheaper liquid hydrocarbons with a wider range in specific gravity might be used, such as gasoline, heavier petroleum ethers etc.

The results show that the separation of Precipitates No. 2



and 3 is not entirely satisfactory. It appears that in some cases portions which ought to be in 2 are carried over into 3. Further experimentation might hit upon a precipitating liquid which would give a sharper separation than methyl alcohol gives.

If the investigator objects to carbon disulphide for any reason chloroform may be used in its place as it is more pleasant to work with.

It is highly desirable to extend this method to use with other kinds of asphalt and find out if it is generally applicable, which we think will prove to be the case.

We are comparing the results from this method with results from others to see how our Precipitates 1, 2 and 3 compare with the " Petrolene," " Asphaltene," Malthene," Carbene," etc obtained by other investigators and trying to find out if possible factors for transferring one to the other if there is a constant relation.

In conclusion then, we consider the method very valuable for determining the constituents of asphaltic substances and an improvement for that purpose over methods formerly used, in that, it saves time and gives more concordant results. More investigation, however, is necessary to develop further possibilities of the method and to perfect it.

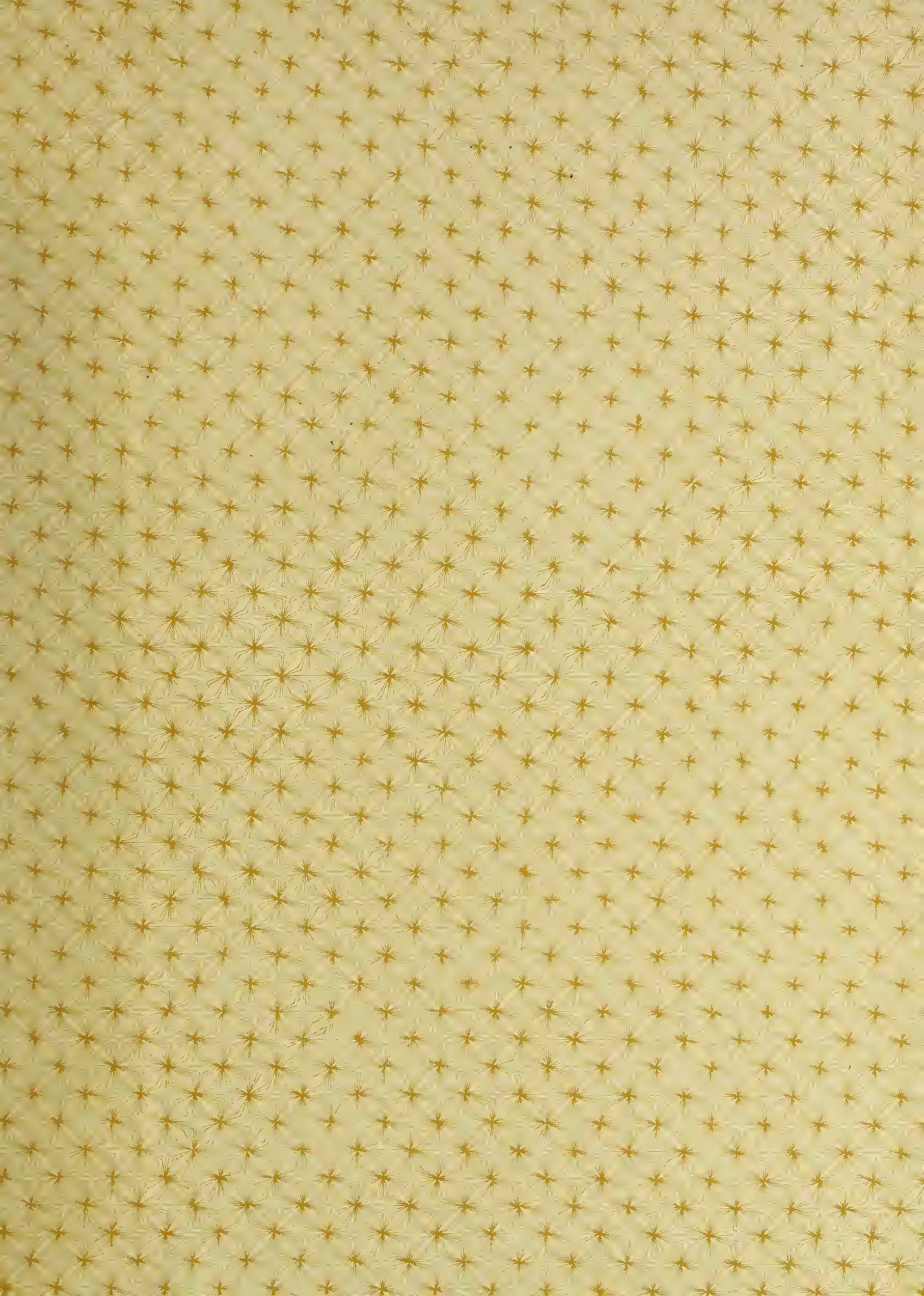
We wish to express our appreciation for materials furnished us gratuitously by the Standard Asphalt and Rubber Company, Barber Asphalt Company and Standard Oil Company.



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